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Diffusion in a strongly correlated 2D liquid system

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Abstract Two-ionic model for 2D aqueous electrolytes is modified to make it compatible with the real physical systems by the introduction of grand canonical sampling for many ion systems. The interacting particles are represented by charge distribution with nonzero charge, dipole and quadrupole moments. The possible interactions existing in the system are charge-charge, charge-dipole, charge-quadrupole and dipole-dipole. Analysis of the obtained data is clarified and better understood by comparing it with Arrhenious' form. This points to the restriction in the motion of the ions in two dimension compared to that in three dimension of the same system. The concentration dependence of the diffusion coefficient suggests a structural transition. The Monte Carlo study of the temperature dependence of the diffusion coefficient also indicates the existence of a phase transition. The spurious changes in the diffusion data obtained can be analysed by the conjecture of site blocking. A thorough study and critical analysis of the effect of decreasing temperature on the samples with added cation to limit motions in the 2D system, reveals an interesting information — a signature of glass transition.

Keywords 2D aqueous electrolytes, diffusion coefficients, Monte Carlo simulation, temperature and concentration dependence, glass transition

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1. Introduction

Due to the technological relevance with nuclear medicine and microelectronics [1] in recent years, there has been an explosion of interest in studying the properties of 2D aqueous electrolytes in various fields of colloidal, electrochemical and biological sciences. The structure of such system is poorly understood in the molecular level because of the inherent complexity of the system arising out of the continuously changing arrangement of different types of particles constituting the system and correlations existing between them, For studying the dynamical properties of these systems, diffusion can be used as a tool. But devising experiment to probe the transport mechanism in such system is not straightforward. Even if some techniques [2a] which have already been developed for the 3D liquid systems [2b], can be extended to explore such 2D liquid systems, the experimental results suffer from the lack of supporting theories. The available theory is limited to the phenomenological continuum approach and fails to characterize the complexity of the referred system. Computer simulations being neither experiment nor theory, can take over the task of both. It plays the role of theory for complicated systems like aqueous electrolyte solutions since such systems can not be treated analytically till today.

2. Methodology

It seems quite difficult to tackle a highly correlated 2D liquid system composed of innumerable ions and water molecules. Moreover, there is still no generally agreed structural model of such systems even in 3D. Thus, it is plausible to study aqueous electrolytes by means of non-primitive models in which the solvent is modelled as molecules rather than continuum. One of the simplest non-primitive model is the ion-dipole model, consisting of hard spheres having equal diameters with charges embedded on it in the sea of point dipoles.

The simulation method described in our previous work [3], has been modified to achieve the real physical situation by introducing grand canonical sampling for many ion systems. Since the particles are at liberty to move randomly inside the lattice during simulation, random moves are conducted as a Markov process to generate a sequence of configurations. There are four types of moves in the simulation – displacement, rotation, creation and deletion. Periodic boundary conditions

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are used to minimize the size effect. The number of moves of ions and dipoles are made proportional to their concentrations to reach the equilibrium configuration, the least value for which is 10^5 Monte Carlo steps (MCS) per particle. Due to the long range of Coulomb interaction, the simulation of charged and polar fluids has always been a difficult task and at the same time a finite size effects become a serious problem. Here, Ewald summation [4] is performed to cope up with the situation.

To configure the 2D aqueous electrolyte, m ions and n point dipoles representing water molecules are placed randomly in the lattice sites. Both m and n are varied to generate electrolyte solutions of different concentrations. These particles are at liberty to move randomly inside the lattice. Periodic boundary conditions are used to minimize the size effect. Only the nearest neighbour interactions are considered. The effective interactions existing in the system are charge-charge, charge-dipole, dipole-dipole, and charge-quadrupole. The possible interactions are of the form:

$$\text{Charge} - \text{charge} \quad = \phi_{c,c}(r_{ij}) = q_i q_i \left(|r_{ij}|\right)^{-1},$$

$$\text{Charge} - \text{dipole} \quad = \phi_{c,d}(r_{ij}) = -q_i \mu_i \cdot \nabla \left(|r_{ij}|\right)^{-1},$$

$$\text{Dipole} - \text{dipole} \quad = \phi_{d,d}(r_{ij}) = -\left(\mu_i \cdot \nabla\right)\left(\mu_j \cdot \nabla\right)\left(|r_{ij}|\right)^{-1}$$

$$\text{Charge} - \text{quadrupole} \quad = \phi_{c,q}(r_{ij}) = -q_i \Theta : \nabla\nabla \left(|r_{ij}|\right)^{-1},$$

where r_{ij} is the distance between q_i and q_j the charges at the i-th and j-th sites and double dot is the Chapman Cowling notation used to represent the inner product of two tensors.

The state parameters used in the simulation procedure are listed in the Table 1. The values of μ and q correspond to the dipole moment of water and the charge of the monovalent ion.

Table 1. Parameters used in simulation.

Molecular properties	
Charge of ion	1.6×10^{-19} C
Dipole moment of solvent	1.8 D
Diameter of ion	3.0×10^{-10} m
Configuration of sampling parameters	
Maximum displacement per configuration	0.05 times box length
Maximum rotation of dipole per configuration	4.5° in θ
Real space cut-off distance R_{cut}	5σ, 7σ, 7.5σ, 10σ
Ewald sum parameter	
α convergence parameter	2.8
K_{max} cut-off in real space	3.0
State parameters	
Temperature	298.15K
Reduced density ρ	Varied from 0.6
Reduced charge q	8, 13.6
Simulation conditions	
Number of ions	Varied from 2 to 38 depending on total % filling of lattice
Number of dipoles	Varied from 20 to 68 depending on total % filling of the lattice

3. Results and discussion

The surface diffusion coefficients (D) of the positive charges have been calculated over the Monte Carlo temperature T_m ranging from 10^{-6} to 10^6 for a wide range of values (Figure 1). The spurious changes in diffusion data obtained at some particular situation can be rationalized by the conjecture of site blocking. For a better understanding, a detailed study of the effect of decreasing temperature on the samples with added cations and anions to limit the motions in the structures, has been carried out. A thorough study of the variation of the diffusion coefficient for a two ionic system with increasing water number density, reveals that the transition temperature increases with the increase of percentage filling in lattice. Any of the plots of Figure 2 presents a typical variation of the 2D diffusion data with $\log T_m$. In the range –6 to +6, D values show a sharp minimum at $T_m = T_c$. This sharp fall of diffusivity points to the ultraviscosity of the system which is supported by the similar signature of anomalous rise of viscosity accompanied by the depression in diffusion data for similar 3D system [5]. Moreover, such ultraviscosity has already been reported [6] for bulk water at atmospheric pressure on cooling. Actually, aqueous systems close to freezing point, has a local structure similar to solid but in its equilibrium configurations, there are some concentrations of dislocations which can not move to the surface under the influence of an arbitrarily small shearing stress and produce viscous flow [7] whereas in the solid state, there is no free dislocation in equilibrium and so the system is rigid. It has been found that the spectrum of data obtained, can be clarified and

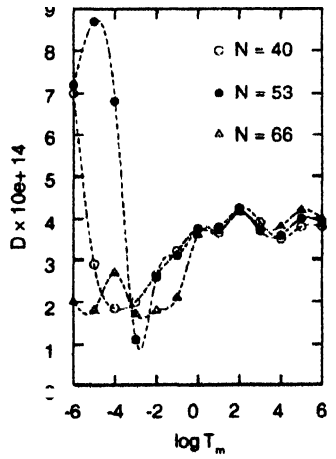

Figure 1. Variation of surface diffusion coefficient with MC Temperature T_m.

better understood by comparing it with the diffusion coefficients typically expressed in the Arrhenius' form, $D = D_0 \exp(-E_{diff}/kt)$ cm^2/sec, where E_{diff} is the activation energy. So the motion in 2D system is more restricted compared to that in the 3D of the same sample. All these facts points to the occurrence of a glassy state at or in the neighbourhood of T_c and the transition occurring at T is a glass transition.

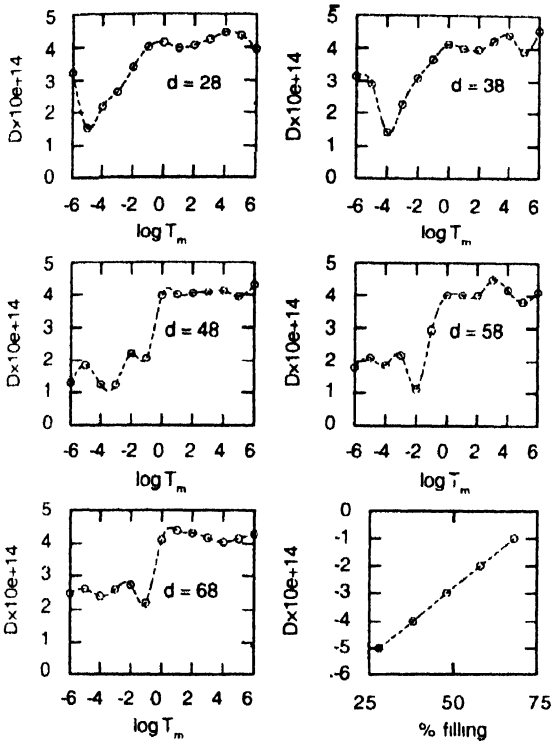

Figure 2. Variation of surface diffusion coefficient with dipole number density for a 2-ionic system.

The nature of variation of diffusion coefficient below and above critical point is just reverse. A thorough investigation on the T_c over the variation of lattice configuration is studied by variation of –

(i) dipole number density for a 2-ionic system (Figure 2) and

(ii) percentage filling of the lattice keeping the ion:water (dipole) number density 1:1 (Figure 3),

reveals many interesting facts. A linear decrease in the value of $\log T_c$ is observed with the increase in the % filling of the lattice. Our earlier data of comparatively simpler model also fall on this straight line suggesting the coherency between the two. The second set of concentration dependence of surface diffusion coefficient with increase of packing density reveals the occurrence of another transition. It is interesting to note that this transition temperature also varies linearly with the % filling for lowest packing density and the rate of variation gradually falls as the packing density increases and attains a fixed value of 10^{-5} for all other % filling when the packing density is 66.66%.

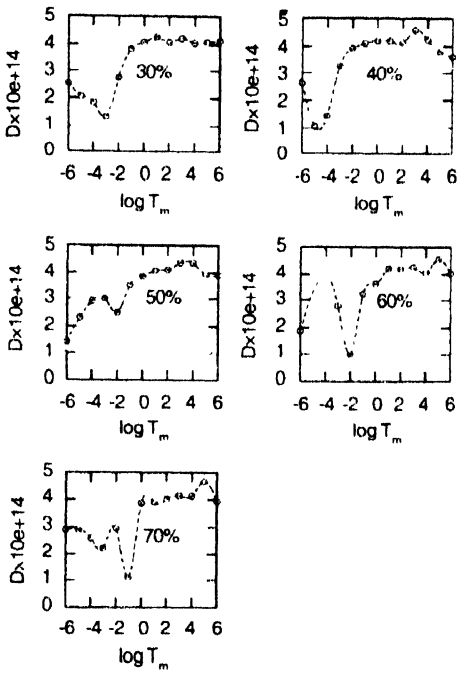

Figure 3. Variation of surface diffusion coefficient with percentage filling of the Lattice (ion water number density 1 1)

Moreover, diffusion coefficients obtained from Monte Carlo study and experiments reveal interesting and worth pursuing features regarding phase transition. To be more specific, the experimental data is suggesting a structural transition. However, a thorough analysis of the experimental data requires information regarding the short time dynamics and structures of interlayer water molecules in aqueous electrolytes. With a view to characterize the different transitions and to understand the dynamics of the 2D aqueous electrolytes in the glassy state, a freezing criterion based on the structural properties of 2D dense fluids using L-J potential is being investigated.

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